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Coordination Chemistry Reviews 249 (2005) 1857–1869

COORDINATION CHEMISTRY REVIEWS

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Review

The coordination chemistry and reactivity of group 13 metal(I) heterocycles

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Received 14 September 2004; accepted 24 December 2004
Available online 8 February 2005

Contents

Abstract

This article summarizes the synthetic strategies that have been used to prepare anionic five-membered and neutral six-membered heterocycles containing a group 13 metal in the +1 oxidation state. In addition, a survey of the coordination chemistry and reactivity of these species is described, drawing comparisons with the well known *N*-heterocyclic carbene class of ligand where possible. Computational studies of the free heterocycles and their complexes are also reviewed.

Keywords: Group 13; Low oxidation state; Heterocycle; Carbene analogue

1. Introduction

The study of low oxidation state aluminium and gallium chemistry has rapidly expanded over the last decade and has produced some of the most remarkable results in the history of main group chemistry. Of particular note is the work of Schnöckel et al. who have developed a specialised reactor to produce multi-gram quantities of “metastable” aluminium(I) and gallium(I) halides which are stabilised by coordination with ether or amine Lewis bases, $[\{MX(L)\}_n]$, M = Al or Ga; X = Cl, Br or I; L = amine or ether. These oligomeric complexes have proved invaluable as precursors to a remarkable array of fascinating sub-valent metal halide, amide, phosphide, silyl and alkyl cluster compounds which challenge existing theories of bonding in p-block clusters [1]. Metastable group 13 metal(I) halides have also been utilised to prepare metal(I) alkyls (group 13 diyls), $(MR)_n$, R = bulky alkyl, aryl, etc., the nuclearity of which depends upon the steric bulk of the alkyl/aryl substituent and the metal involved. These

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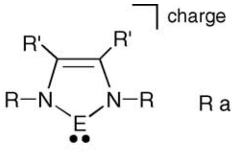
doi:10.1016/j.ccr.2004.12.016

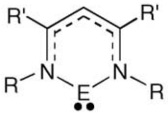
compounds are also accessible via metathesis reactions involving Green's "GaI" reagent or reduction of metal(III) complexes, RMX_2 [2]. In their monomeric state, group 13 diyls, MR, have sp-hybridised metal centres with a singlet lone pair of electrons and two empty p-orbitals. As a result, they have the potential to act as strong σ-donor ligands by utilising their lone pair, whilst their empty p-orbitals could possibly participate in π-back-bonding from suitable filled transition metal d-orbitals. In this respect, group 13 diyls could be thought of as analogues of CO or acyclic carbenes. In practice, these compounds have been employed as both terminal and bridging ligands in a wide variety of transition and main group metal complexes [2,3]. The degree of back-bonding in these complexes has been a controversial issue, perhaps best exemplified by the iron–gallium diyl complex, $[(Ar^*Ga)Fe(CO)_4]$, $Ar^* = C_6H_3(C_6H_2Pr^i_3\text{-}2,4,6)_2\text{-}2,6$, which has alternately been described as containing an iron–gallium triple [4] or single bond [5]. Numerous theoretical studies on this and related complexes have since been carried out and it is now generally accepted that the degree of metal–metal back-bonding is minimal due to the relatively high energy of the group 13 metal p-orbitals [6]. This is, however, not always the case as in homoleptic complexes, e.g. $[Ni\{GaC(SiMe_3)_3\}_4]$, where the diyl ligand does not compete with other ligands for π-electron density, significant π-back-bonding has been calculated [7].



1

E = group 13 element, charge = -1
E = group 14 element, charge = 0
E = group 15 element, charge = +1

R and R' = alkyl, aryl or H



2

E = group 13 metal

Like group 13 diyls, the now well established *N*-heterocyclic carbene (NHC) class of ligand, **1**, E = C, have singlet lone pairs and act as strong σ-donors towards a wide variety of s, p and d-block metal fragments [8]. In NHC-transition metal complexes the p-orbital at the carbene centre is not thought to engage in π-bonding with filled metal d-orbitals to any extent. This is believed to arise from a significant overlap of the nitrogen p-orbital lone pairs with the carbene p-orbital [8]. The electronic and steric properties of NHCs have lent them to a variety of applications in synthesis and catalysis where they are often thought of as phosphine mimics. Considerable attention has also been paid to the heavier group 14 analogues of NHCs, **1**, E = Si, Ge or Sn, which in the case of the silicon and germanium heterocycles, have been used as ligands in the formation of an ever increasing number of complexes [9]. In addition, several valence isoelectronic, cationic phosphorus, arsenic and antimony analogues of NHCs, **1**, E = P, As or Sb, have been reported [10]. A small number of complexes derived from the cyclic phosphenium cations have come forward [11] but no cyclic arsenium or stibenium complexes have been structurally characterised to date. This article reviews the synthesis, stabilisation, coordination chemistry, reactivity and theoretical aspects of anionic five-membered group 13 analogues of NHCs, **1**, E = group 13 metal. In addition, it treats the chemistry of closely related neutral six-membered heterocycles that contain a group 13 metal in the +1 oxidation state, **2**. Several review articles [12–15] have previously discussed aspects of the chemistry of the neutral six-membered heterocycles and, thus, their chemistry will not be comprehensively treated here. Throughout this review, the chemistry of five- and six-membered group 13 metal(I) heterocycles will be compared with that of NHCs and acyclic group 13 diyls.

2. Computational studies of free heterocycles

Two papers detailing theoretical studies of anionic group 13 NHC analogues have appeared. Schoeller and co-workers carried out density functional theory (DFT) calculations at several levels of theory on the heterocycles, $[:E\{N(H)C(H)\}_2]^-$, **3**, E = B, Al, Ga and In [16]. These suggest that all should be stable species with essentially sp-hybridised group 13 centres. The singlet–triplet energy separations of the heterocycles' lone pairs are sizeable (as is the case with NHCs) and thus each possesses a singlet lone pair which is associated with its HOMO. The p-orbitals at E, orthogonal to the heterocycles' planes, are associated with their LUMOs. Significant differences were seen between the electron distributions within the boron heterocycle and the heavier metal analogues. These distributions were analysed using natural bond orbital (NBO) calculations which showed that when E = B, the N–B bonds are largely covalent (Wiberg bond index, 0.889) and the boron centre has a partial negative charge. On going to Al and the heavier group 13 metals the directionality of the non-bonding lone pair and the order of the E–N bonds significantly decrease (E = Al; Wiberg bond index, 0.488). In addition, the metal centres take on a partial positive charge, thus increasing the p-electron density at the nitrogen centres. These calculations also suggest that when E = Al–In, the structure of the heterocycle can best be formulated as a donor–acceptor interaction of E^+ and a chelating diamido unit (Fig. 1). This situation arises from the electronegativity differences between N and E which lead to little delocalisation over the NEN fragment. This is in stark contrast to the significant delocalisation over the NCN fragment of NHCs [8].

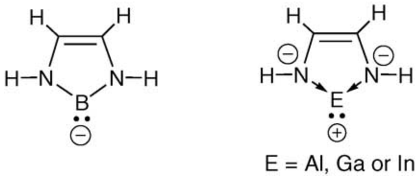


Fig. 1. Representation of the charge distribution in **3**.

Similar results have been obtained using ab initio calculations on the boron and aluminium hetereocyclic anions, $[:E\{N(H)C(H)\}_2]^-$, E = B or Al [17], the calculated geometries of which were found to mirror those reported by Schoeller and co-workers [16]. This study also included a treatment of the stabilising effect of electron delocalisation into the diazabutadiene (DAB) backbone of the heterocycles. It was found that there is appreciable aromatic stabilisation in both ring systems, though the heterocycle with E = B has a significantly greater aromatic ring current than its aluminium counterpart. Saying this, both heterocycles display considerably less aromatic stabilisation than the parent *N*-heterocyclic carbene, $:C\{N(H)C(H)\}_2$, at the same level of theory. Finally, a molecular orbital treatment of the heterocycles established that their HOMOs incorporate singlet lone pairs at either the B or Al centre.

In an extension to their theoretical studies on **3**, the group of Schoeller has recently investigated the stabilisation of anionic group 13 carbene analogues, $[:E\{P(H)C(H)\}_2]^-$, **4**, E = B, Al and Ga, utilising the parent diphosphabutadiene (DPB) in the heterocycle backbone [18]. Using quantum chemical calculations at density functional level it was found that the P–E bonds in **4** are more covalent than the E–N bonds in **3** due to the lower electronegativity of phosphorus relative to nitrogen. In addition, for the metallic group 13 elements the singlet ground states of **4** are considerably more stabilised than those for **3**. Moreover, the electron affinities for the DPB backbones in **4** are larger than those calculated for the DAB fragments in **3**. As a result, the authors suggested that anions related to **4** but with suitably bulky P-substituents, should be experimentally accessible. This prospect is not inconceivable when it is considered that a variety of sterically hindered DPB ligands are now available to the synthetic chemist [19].

The neutral six-membered heterocycles $[:E\{[N(R)C(R')]_2CH\}]$ E = B, Al, Ga, In or Tl; R = H, Me or $C_6H_3Pr^i_2$-2,6 (Ar); R′ = H or Me, have also been the subject of several theoretical studies. The most comprehensive of these employed a number of computational techniques and found that the calculated geometries of the heterocycles with E = Al or Ga compare favourably with the experimentally observed systems (vide infra) [20]. In addition, it was established that when E = Al–In, the metal carries a partial positive charge and the N–E bonds have a substantial ionic character. This is in contrast to the ring with E = B which has a partial negative charge at boron and much more covalent E–N bonds. Electron localisation function (ELF) calculations were carried out to visualise the lone pair on the group 13 element, and these revealed that there is a stereochemically active electron pair in all heterocycles. In addition, the heterocycles' singlet–triplet energy gaps were calculated and for E = B it was found to be small (ca. 20 kJ/mol), whereas for the higher homologues the gap is substantial (>150 kJ/mol). Finally the reactivity of these compounds towards the electron donating NH_3 and electron accepting BF_3 fragments was investigated. For E = Al–In, they act as Lewis acids if NH_3 approaches from above the heterocycle plane, whilst a ring rearrangement reaction occurs for E = B. Most of the ring compounds form a complex with BF_3 which lies in the plane of the heterocyclic system, as expected. However, due to the increased s character of the metal lone pair on descending the group, the Lewis base character of the heterocycles is reduced to a point where for E = In there is no donor–acceptor bond formed. From these calculations, it was concluded that for E = Al–In, the best representation of the heterocycles is a donor–acceptor structure between an anionic chelating β-diketiminato ligand and a positively charged metal centre in the +1 oxidation state (cf. **3**). For the boron ring, a diradical species with a B(II) centre is the best description. This implies that the latter systems will be too reactive to be isolated under normal conditions.

The results of this theoretical study are largely consistent with another preliminary ab initio investigation of the aluminium(I) heterocycle, $[:Al\{[N(Me)C(Me)]_2CH\}]$, which suggests the lone pair at aluminium resides in an sp-like orbital and is stereochemically active [21]. In addition, Power and co-workers have examined the model gallium ring, $[:Ga\{[N(Me)C(Me)]_2CH\}]$, the HOMO of which corresponds to the Ga lone pair, though the LUMO does not involve the Ga p-orbital orthogonal to the heterocycle plane [14]. Instead, this is represented by the LUMO + 1 level and is separated from the HOMO by ca. 110 kcal/mol. The analogous aluminium ring was calculated to have a smaller HOMO–LUMO + 1 gap (by ca. 12 kcal/mol) but in both the separations were large enough to suggest that experimental examples of these compounds should act as strong σ-donors but should be poor π-acceptors.

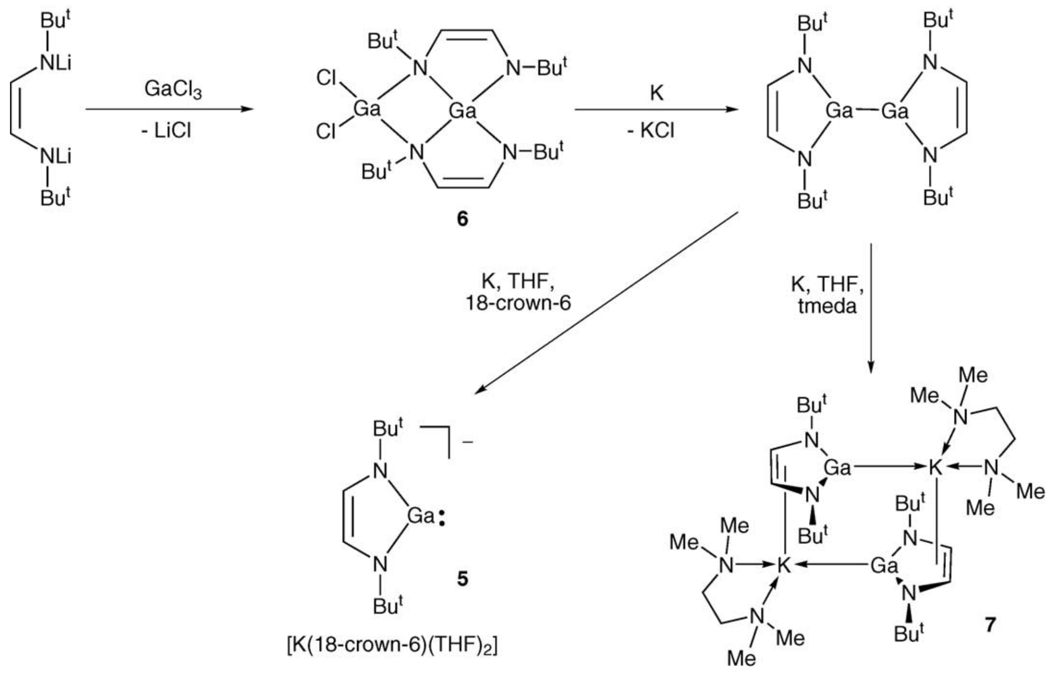
Hill et al. have similarly investigated the indium(I) and thallium(I) heterocycles, $[:M\{[N(Ar)C(R)]_2CH\}]$ M = In, R = Me or CF_3; M = Tl, R = Me; by DFT calculations and found that in the In systems, the HOMO corresponds to the In lone pair which is largely sp-hybridised, the LUMO + 1 is represented by the empty metal p-orbital, whilst the LUMO has largely ligand π^*-character [22]. The HOMO–LUMO + 1 gap for both systems (98.5 and 104.8 kcal/mol, respectively) was calculated to be similar to that found for $[:Ga\{[N(Me)C(Me)]_2CH\}]$. Perhaps not surprisingly, calculations for the thallium(I) β-diketiminate complex, $[:Tl\{[N(Ar)C(Me)]_2CH\}]$, pointed towards a significant re-ordering of orbital energies in that the HOMO is entirely ligand based, the metal lone pair is located in an orbital 17 kcal/mol lower in energy than the HOMO, and the LUMO contains the empty p-orbital at the thallium centre.

3. Synthesis and structure of free heterocycles

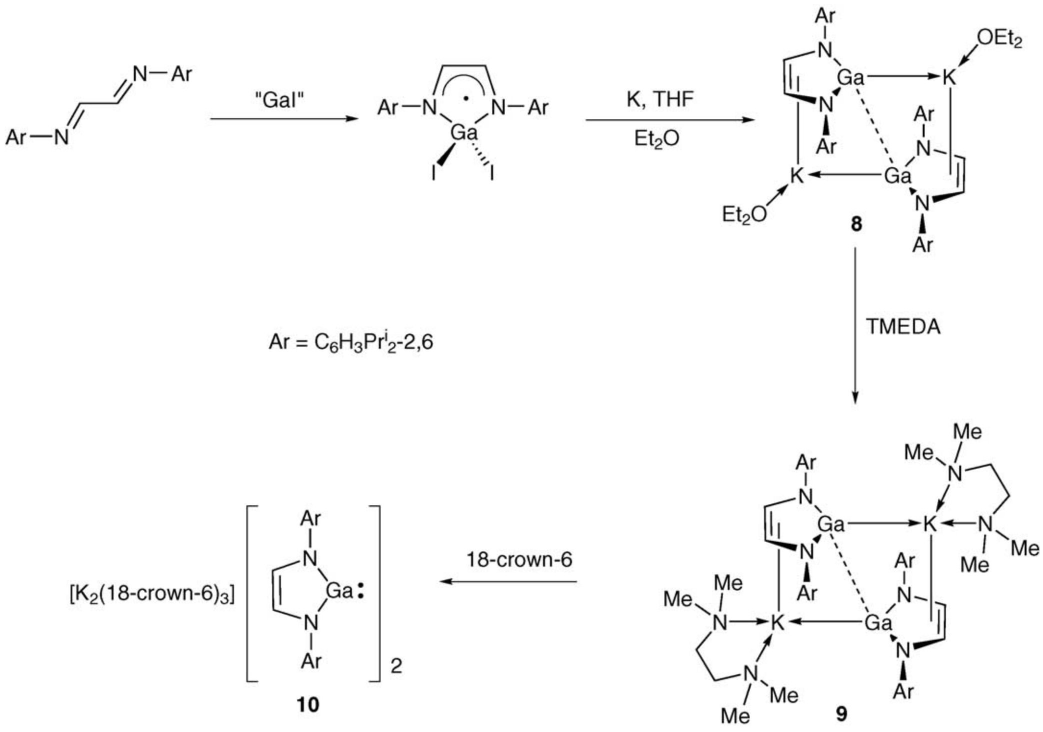
3.1. Synthesis and structure of anionic five-membered heterocycles

At present, there are no known examples of the anionic heterocycles, **1**, with E = B, Al, In or Tl. Synthetic strategies to two examples of **1**, E = Ga, have been developed and both require the inclusion of sterically bulky *N*-substituents to kinetically stabilise the ring systems. The first reported synthesis of an anionic gallium *N*-heterocyclic carbene analogue, **5**, appeared from the group of Schmidbaur et al. as recently as 1999 [23]. The synthesis is shown in Scheme 1 and involves the treatment of a dilithiated diazabutadiene ligand with GaCl$_3$ to give a chlorogalla-imidazole, **6**. This was reduced in two steps over 5 days with potassium in the presence of a crown ether to give **5** as a potassium salt in poor yield (4%). When the reduction was carried out in the presence of tmeda instead of 18-crown-6, complex **7** was isolated in an 18% yield after 14 days [24]. It is worthy of note that the digallane intermediate had previously been reported by Cowley and co-workers [25]. Both salts were structurally characterised and **5** showed no cation–anion contacts. The heterocycle is virtually planar with an N–Ga–N angle of 81.8(3)°, Ga–N bond lengths of 1.985(6) Å and a C–C bond length of 1.380(6) Å. These metric parameters compare favourably with those calculated for the previously mentioned model systems and suggest a small degree of ring delocalisation and aromaticity. Complex **7** is dimeric in the solid state and can be considered as consisting of monomeric units which comprise a gallium heterocycle η^5-coordinated to a K(tmeda) fragment. An intermolecular interaction of the gallium lone pairs with potassium centres aggregates these monomeric units into centrosymmetrical dimers. The intra-ring parameters are similar to those in **5** and the intermolecular Ga–K contact is 3.468(1) Å. A line connecting the Ga and K centres forms an angle of 20.8° with the C$_2$N$_2$Ga ring plane, indicating that the lone pair of electrons at the gallium atom is orientated towards the potassium counterion.

We have reported higher yielding syntheses (ca. 75%) of two potassium complexes, **8** and **9**, incorporating an anionic gallium heterocycle, **10**, with bulkier 2,6-diisopropylphenyl substituents at the nitrogen centres (Scheme 2) [26]. This route involves the use of “GaI”, the preparation of which was first reported by Green et al. in 1990 [27]. The formulation of this reagent is not totally clear but it has been shown to act as a source of Ga(I) and one Raman spectroscopic study has pointed to it existing as [Ga$^+$]$_2$[Ga$_2$I$_6$]$^{2-}$ [28]. The reaction of {(Ar)N=C(H)}$_2$, Ar–DAB (Ar = 2,6-diisopropylphenyl), with “GaI” led to a one-electron reduction of the DAB ligand, a disproportionation and the formation of a paramagnetic Ga(III) compound [29] which was cleanly reduced by excess potassium in Et$_2$O to give **8** in a 75% yield. The crystal structure of **8** showed it to be very similar to that of **7**. However, whilst the geometries of the GaN$_2$C$_2$ rings, the Ga → K bond lengths and the η^5-Ga-heterocycle interactions mirror those of **7**, there are significant differences. For example, the Ga → K bond in **8** forms an angle of only 3.4° with the C$_2$N$_2$Ga ring plane (cf. 20.8° in **7**). This in turn means that the distance between the Ga centres in **7** is 4.21 Å, whereas in **8** it is only 2.8640(13) Å. The short interaction is outside the upper limit of the normal range for Ga–Ga single bonds, but it was suggested that it could point towards the two centres being held together, not only by an electrostatic



Scheme 1.

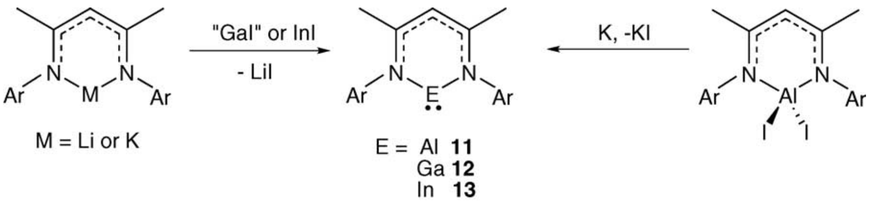


Scheme 2.

attraction to the potassium centres but also by a partial donation of electron density from the lone pair on each gallium centre into the empty p-orbital on the other. This situation can be compared to the Sn–Sn interactions in trans-bent distannenes, $R_2Sn{=}SnR_2$, for which two similar donor–acceptor bonds have been implicated [30]. Interestingly, treatment of **8** with tmeda led to **9** which is a direct analogue of **7** but also displays a short Ga–Ga separation, 2.8746(15) Å. This interaction cannot be very strong as removing the coloumbic assistance provided by the potassium counterions by treating **8** with 18-crown-6 led to the free anionic heterocycle, **10**, as an ion separate salt.

3.2. Synthesis and structure of neutral six-membered heterocycles

The syntheses of the neutral six-membered heterocycles, **11**–**13**, have been achieved using two general synthetic routes (Scheme 3). The thermally stable (dec. > 150 °C) aluminium heterocycle was prepared in a 21% yield via a potassium reduction of an Al(III) precursor [21]. Both the Ga (39%, m.p. 202°) [31] and In (36%, photolabile) [32] ring systems were synthesised in salt elimination reactions between the β-diketiminate anion and the appropriate metal(I) iodide. It is noteworthy that a previous attempt to prepare **13** by this method but using InCl was not successful [33]. The crystal structures of all three complexes are isomorphous and show well-separated monomeric units with geometries close to those predicted by theoretical studies on model compounds. The E–N bond lengths and N–E–N angles are significantly longer and more acute, respectively, compared to values seen in related β-diketiminato group 13 metal(III) complexes. These observations have been ascribed to the larger covalent radii of the group 13 metals in their +1 oxidation states. This trend continues in the homologous Tl(I) complex, $[:Tl\{[N(Ar)C(Me)]_2CH\}]$ [22], and several other closely related heterocycles, $[:Tl\{[N(R)C(R')]_2CR''\}]$ R = Ar or $SiMe_3$; R′ = Me, Bu^t, Ph or H; R″ = H or Ph; the syntheses and structural characterisations of which have recently been reported [34].



Scheme 3.

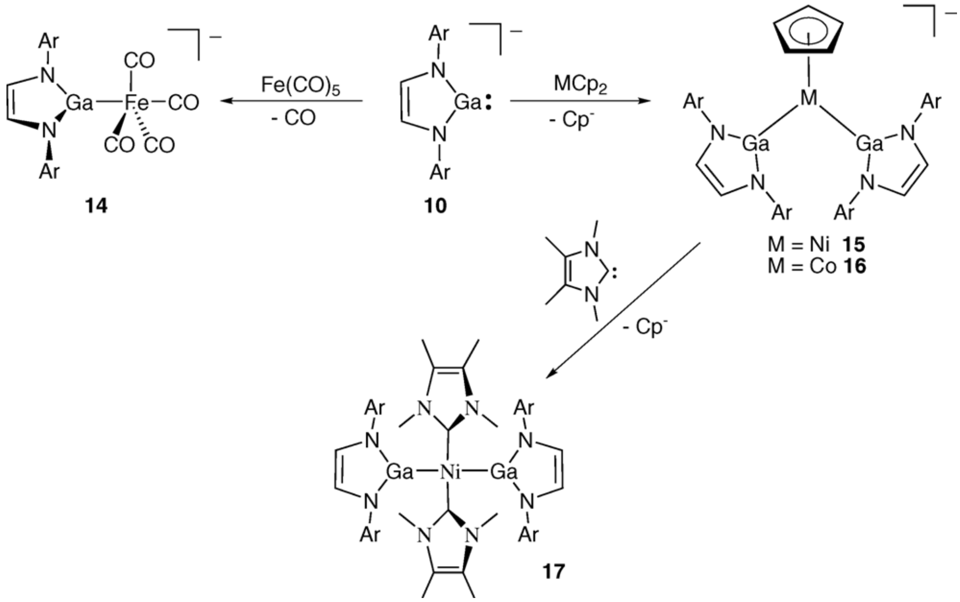
4. Reactivity of group 13 metal(I) heterocycles

4.1. Reactions of anionic five-membered heterocycles with transition metal precursors

No metal coordination chemistry has been reported for the *tert*-butyl substituted gallium heterocycle, **5**. In contrast, we have embarked on a systematic study of the coordination chemistry of the bulkier **10** towards both transition and main group metal fragments. Throughout this work we have aimed to assess any analogies between **10** and its valence isoelectronic *N*-heterocyclic carbene counterparts in terms of its reactivity and the properties of its complexes. Although only in its infancy, this study is highlighting similarities, but also significant differences between **10** and NHCs.

As with NHCs, the heterocycle, **10**, readily reacts with binary metal carbonyl compounds via CO displacement. For example, when **10** was treated with $Fe(CO)_5$, complex **14** was formed in moderate yield (54%) (Scheme 4) [35]. The facile nature of the CO displacement reaction is consistent with the strong σ-donor nature of the heterocycle. The crystal structure of **14** revealed it to be polymeric, through bridging potassium centres coordinated by a molecule of tmeda, two equatorial carbonyl oxygens and an η^2-interaction to one of the heterocycle's arene substituents. Not surprisingly, its three-coordinate Ga–Fe bond length [2.3068(8) Å] is significantly longer than that in the related diyl complex $[(Ar^*Ga)Fe(CO)_4]$, $Ar^* = C_6H_3(C_6H_2Pr^i_3\text{-}2,4,6)_2\text{-}2,6$, [2.248(7) Å] which possesses a two-coordinate Ga centre [4]. The positions of the CO stretching frequencies in the infrared spectrum of **14** were thought to be suggestive of negligible back-bonding from iron d-orbitals into the Ga p-orbital LUMO of the heterocycle. This is perhaps not surprising considering the high energy of the LUMO and the fact that it would be competing for d-orbital electron density with a *trans*-carbonyl ligand. A DFT study of a model of this complex, $[Fe(CO)_4\{Ga[N(H)C(H)]_2\}]^-$, using the Charge Decomposition Analysis (CDA) technique [6] confirmed the lack of π-character in the Fe–Ga bond, as the ratio of its σ/π-character was found to be 3.40. Interestingly, this is very close to that in the model NHC complex, $[Fe(CO)_4\{C[N(H)C(H)]_2\}]$ ($\sigma/\pi = 3.39$). In addition, a natural bond orbital (NBO) analysis of the model anion showed a significant development of positive charge at the gallium centre, relative to the free heterocycle which is in line with a significant loss of electron density from the gallium centre upon coordination. Finally, the dissociation energy for the Fe–Ga bond D_e (94.0 kcal/mol) was found to be higher than the dissociation energies for the Fe–C bonds in the NHC complex ($D_e = 64.9$ kcal/mol) and $Fe(CO)_5$ ($D_e = 52.2$ kcal/mol). This observation was said to be consistent with the facile formation of **14**.

The preparation of a complex of **10** with a carbonyl free late transition metal fragment could potentially lead to more substantial metal–Ga back-bonding than was observed in **14**. This has been achieved with the treatment of the metallocenes Cp_2M (M = Ni, Co) with two equivalents of **10** which resulted in moderate yields of complexes containing the anions, **15** and **16** (Scheme 4) [36]. Their formation arises from KCp elimination reactions which are closely related to reported reactions of NHCs with transition metal metallocenes. These have been shown to give cationic complexes, $[CpM(NHC)_2]^+$, via Cp anion displacement reactions [37]. The structure of **15** disclosed very short Ni–Ga bond lengths (2.218 Å, avg.) which are only longer than those in the homoleptic gallium diyl complex,



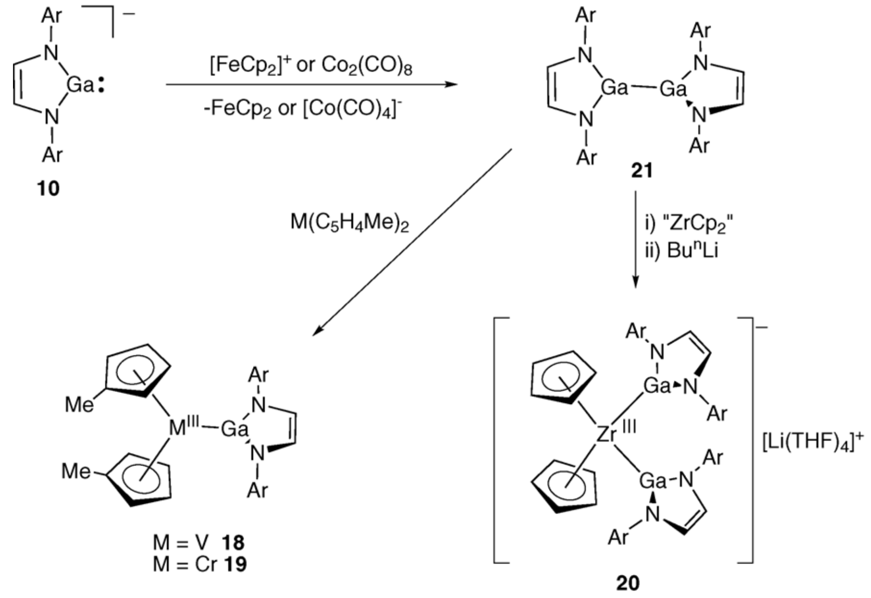
Scheme 4.

$[\mathrm{Ni}\{\mathrm{GaC(SiMe_3)_3}\}_4]$ [2.1700(4) Å], for which significant Ni–Ga back-bonding has been suggested [7]. As a result, a model of **15**, $[\mathrm{CpNi}\{\mathrm{Ga[N(Ph)C(H)]_2}\}_2]^-$, was examined by an established DFT technique using the Amsterdam density functional (ADF) code and found to have an optimised geometry very close to that in the experimental compound. In addition, the theoretical study gave a value of 28% for the π-component of the Ni–Ga bonds [38], which is considerably greater than that in $[\mathrm{Fe(CO)_4}\{\mathrm{Ga[N(H)C(H)]_2}\}]^-$ and related dihaloboryl complexes, $[\mathrm{L}_n\mathrm{MBX_2}]$ [39], but cannot be considered as substantial.

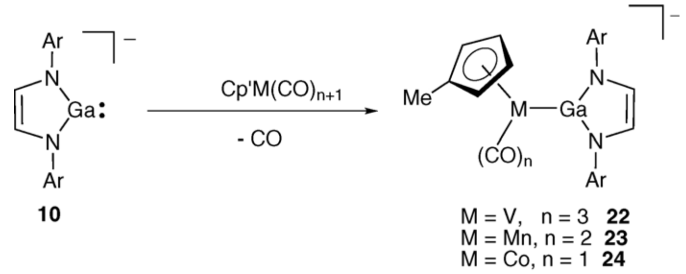
The anion, **15**, is unreactive towards **10** but was found to react with the NHC,:C{N(Me)C(Me)}$_2$, to give the novel, neutral complex, **17**, which has no precedent in gallium diyl chemistry (Scheme 4). Interestingly, the Ni–Ga bond lengths in this compound are ca. 0.11 Å longer than in **15**. This is thought to be due to the *trans*-disposition of the apparently highly nucleophilic gallium heterocycles.

Although not prepared directly from the gallium heterocyclic anion, **10**, several neutral or anionic gallyl complexes of metallocenes (e.g. **18**–**20**) which are closely related to **15**, have been synthesised and studied (Scheme 5) [40]. Their preparations have been facilitated by the discovery that the reaction precursor, a digallane, **21**, can be prepared in high yield via the oxidative coupling of **10** with either $[\mathrm{Cp_2Fe}][\mathrm{PF_6}]$ or $[\mathrm{Co_2(CO)_8}]$, the by-product in the latter process being $\mathrm{K[Co(CO)_4]}$ [41]. It is significant that related reactions of NHCs with $[\mathrm{Co_2(CO)_8}]$ lead only to CO displacement and the formation of complexes of the type, $[\mathrm{Co_2(CO)_6(NHC)_2}]$ [42]. In contrast, the reactions of NHCs with the ferrocenium cation do mirror the formation of **21** in that they lead to oxidative coupling of the NHC [43]. It is noteworthy that **21** has also been prepared by the photolysis of a galladiazole, $[(\eta^1\text{-Cp}^*)\mathrm{Ga}\{\mathrm{N(Ar)C(H)}\}_2]$ [44]. The mechanism of formation of **18**–**20** is thought to involve an oxidative insertion of the metallocene into the Ga–Ga bond of **21** to give the transient intermediates, $[\mathrm{Cp^R}_2\mathrm{M^{IV}}\{\mathrm{Ga[N(Ar)C(H)]_2}\}_2]$, $\mathrm{Cp^R} = \mathrm{C_5H_4Me}$ or $\mathrm{C_5H_5}$. In the case of the intermediates with M = V or Cr, subsequent comproportionation reactions with excess metallocene gave **18** and **19**, respectively. When M = Zr, reduction of the intermediate to the Zr(III) complex, **20**, seemingly occurs with Bu^{n}Li which was present in the reaction mixture as a reagent to generate "ZrCp$_2$" in situ. All complexes **18**–**20** are paramagnetic and have magnetic moments and EPR spectra expected for d^1, d^2 or d^3 metal centres. The X-ray crystal structures of **18** and **19** are isomorphous and that of **18** exhibits the first example of a structurally characterised V–Ga bond [2.530(1) Å] which can be compared with the shorter Ga–Cr separation in **19**, [2.4231(11) Å]. The crystal structure of **20** exhibits only the second examples of structurally characterised Zr–Ga bonds [2.738 Å, avg.] which were said to be longer than expected due to steric crowding about the Zr centre of the complex.

Since 2000, the use of NHCs as ligands in the formation of complexes with cyclopentadienyl transition metal-carbonyl fragments has expanded. This work has shown that in these complexes there is negligible M-carbene π-back-bonding and, as in other NHC complexes, the carbene ligands can be considered as a phosphine mimics [45]. As a result, the catalytic activity of such complexes is beginning to be explored [46]. Similar chemistry is starting to emerge for the gallium heterocycle, **10**, which has been employed as a ligand in the formation of a series of anionic first row transition metal half sandwich complexes, **22**–**24** (Scheme 6) [38]. The positions of the carbonyl stretching bands in the infra-red spectra of these compounds were found to be at marginally higher frequencies than might be expected if the gallyl ligand was acting solely as a σ-donor and, thus, the nature of M–Ga bonds in



Scheme 5.



Scheme 6.

the model anions, $[CpM(CO)_n\{Ga[N(Ph)C(H)]_2\}]^-$, M = V, Mn or Co; $n = 3$, 2 or 1, was investigated by DFT techniques [39]. These investigations revealed small π-back-bonding contributions to the M–Ga bonds, M = V (12%), Mn (18%), Co (26%), which increase with the electron richness of the transition metal, and as the number of attendant carbonyl ligands decreases. Although small, the level of back-bonding in these complexes is thought to be greater than in analogous neutral NHC complexes.

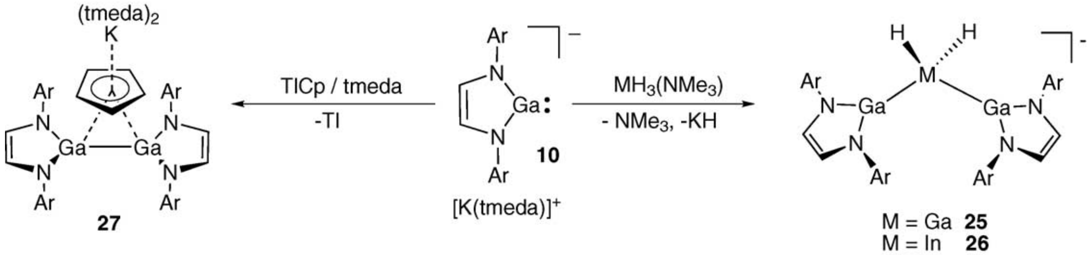
Given that **10** is anionic, one would envisage that its salt elimination reactions with transition metal halide complexes would yield a variety of new gallyl-metal complexes. This is, however, not the case as these reactions are now known to generally proceed via oxidative insertion of the Ga(I) centre of **10** into M-halide bonds with a concomitant reduction of the M center (via electron transfer from the diazabutadiene backbone of the gallium heterocycle) to give intermediates, the M–Ga bonds of which undergo homolytic cleavage, affording further products [38]. For example, in the reaction of **10** with $[Mn(CO)_5Br]$, the paramagnetic gallium(II) dimer, $[\{BrGa[N(Ar)C(H)]_2\}_2]$, is formed in high yield along with several manganese carbonyl products. There is precedent for similar metal–halogen insertion reactions in group 13 diyl-transition metal chemistry [47].

4.2. Reactions of neutral six-membered heterocycles with transition metal precursors

There are only two reported reactions of a six-membered group 13(I) heterocycle with transition metal precursors. In the first, the gallium(I) heterocycle, **12**, was reacted with $Fe(CO)_5$ to form $[(CO)_4FeGa\{[N(Ar)C(Me)]_2CH\}]$, via a CO displacement reaction [48]. This complex is closely related to the anionic compound, **14**, and although both possess three-coordinate gallium centres, the Fe–Ga bond length in the former [2.2851(3) Å] is significantly shorter than that in **14** [2.3068(8) Å]. The positions of the CO stretching absorptions in the infra-red spectrum of $[(CO)_4FeGa\{[N(Ar)C(Me)]_2CH\}]$ were said to suggest negligible π-back-bonding between the Fe and Ga centres. In the second report, **12** was reacted with $[AuCl(PPh_3)]$ in either a 1:1 or 2:1 stoichiometry to yield $[(Ph_3P)Au\{Ga(Cl)\{[N(Ar)C(Me)]_2CH\}\}]$ or [(**12**)Au{Ga(Cl){[N(Ar)C(Me)]$_2$CH}}], respectively, via oxidative insertion of the Ga(I) center of **12** into the Au–Cl bond of the gold precursor [49].

4.3. Reactions of anionic five-membered heterocycles with main group precursors

The reactivity of *N*-heterocyclic carbenes towards main group element precursors is now well established [8]. In the past 2 years, the chemistry of main group complexes of the valence isoelectronic gallium heterocycle, **10**, has begun to emerge and comparisons between the two fields have been drawn. For example, it is known that the steric and electronic properties of bulky NHCs make them excellent ligands for the stabilisation of thermally labile fragments such as the group 13 metal trihydrides. This is probably best exemplified by the complex, $[InH_3\{C[N(Mes)C(H)]_2\}]$, Mes = mesityl, which does not decompose until 115 °C in the solid state. This can be compared with related Lewis base adducts, e.g. $[InH_3(NMe_3)]$, which is unstable above −30 °C [50]. Interestingly, the reactions of **10** with indium and gallium trihydride precursors did not give MH_3 complexes, but instead the novel trimetallic systems, **25** and **26**, were formed in good yields (Scheme 7) [51]. These products were obtained under any stoichiometry of reactants and seemingly arise from a

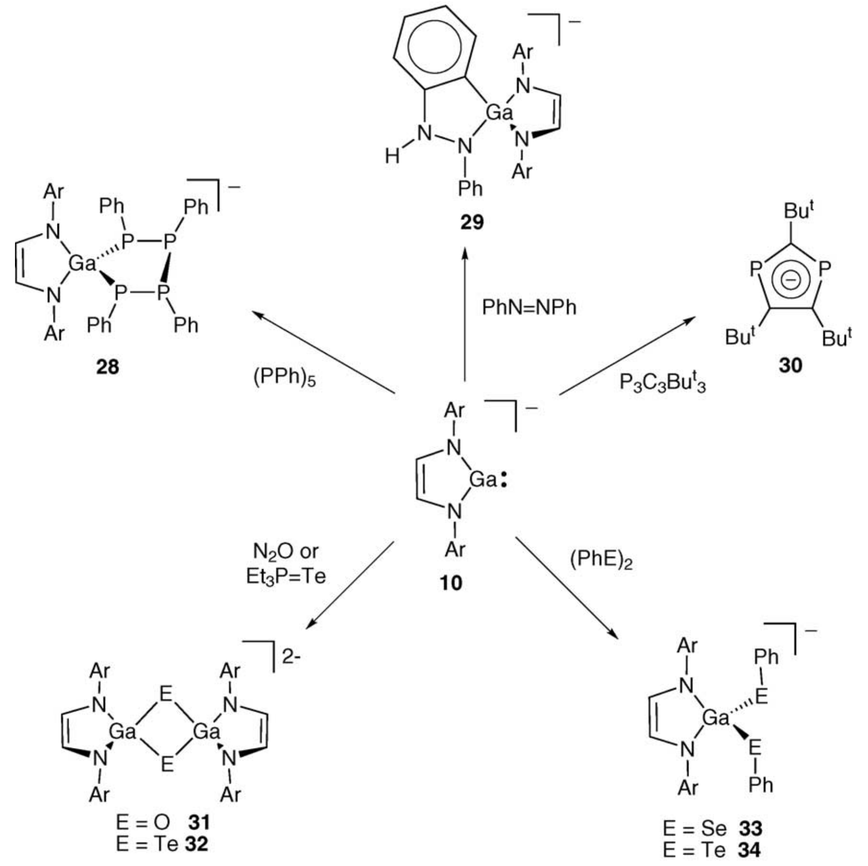


Scheme 7.

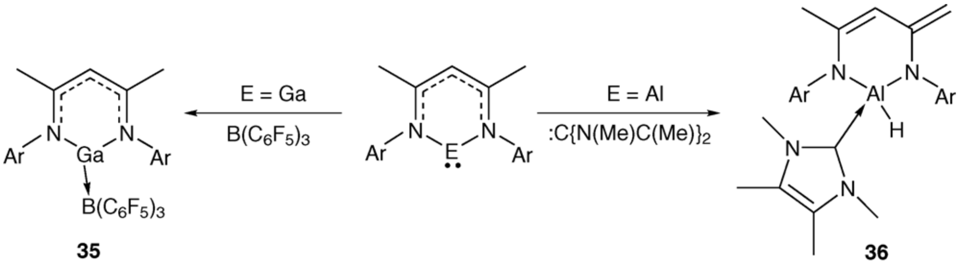
combination of KH elimination and gallium heterocycle coordination reactions. The thermal stability of both is good and it is worthy of note that **26** decomposes at an almost identical temperature (116 °C) to the previously mentioned NHC complex. Both compounds have been structurally characterised, and **26** exhibits the first example of a Ga–In bond. Additionally the Ga–Ga bonds in **25** [2.4071(9) Å] were thought to be strong as they are at the short end of the normal range for such interactions. DFT studies have been undertaken on models of these compounds and they highlight a significant development of negative charge on the central metal atoms relative to the terminal donor Ga centres.

The reactivity of **10** towards main group cyclopentadienyl complexes has begun to be investigated. One report details its treatment with either InCp or TlCp which leads to In or Tl metal deposition and the oxidative coupling of **10** to give the known digallane, **21**. This traps half the generated KCp to give the unusual complex, **27**, in which the Cp^- anion symmetrically bridges the two Ga centres, giving rise to the first example of a π-interaction to a Ga(II) centre (Scheme 7) [41]. It was found that **27** can alternatively be prepared by the direct reaction of **21** with KCp in the presence of tmeda. DFT calculations on a model of the complex, $[\{Ga[N(Me)C(H)]_2\}_2\{\mu\text{-}CpK(NH_3)_4\}]$, revealed a binding energy of the KCp salt to the digallane moiety of ca. 29 kJ/mol and a donation of 0.209 electrons from the π-system of the Cp anion into the empty p-orbitals of the digallane unit. This led to a partial pyramidalisation of the Ga centres relative to those in the free digallane, an observation that is reflected in the experimental crystal structure of **27**.

The reactions of **10** with a variety of group 15 and 16 compounds have been examined (Scheme 8) [38]. With regard to group 15, NHCs have been reported to react with cyclopnictanes, $(RE)_n$, E = P or As, to form compounds of the type $[RP \leftarrow \{C[N(R')C(H)]_2\}]$ which have been formulated as NHC adducts of pnictinidene fragments rather than P=C double bonded phosphaalkenes [52]. In contrast, the reaction of **10** with $(PhP)_5$ did not give an analogous gallium-terminal phosphinidene complex but instead the unusual anionic spirocyclic complex, **28** (yield 22%), apparently via an oxidative insertion of the Ga(I) centre into a P–P bond of $(PhP)_5$ with concomitant loss of one PPh fragment. The related reaction of **10** with azobenzene had a completely different outcome, namely the high yield formation of another anionic spirocyclic system, **29**. This reaction proceeds via an orthometallation of one of the phenyl substituents of the azobenzene with a concomitant hydrogen migration to an *N*-centre of the azobenzene. The only other reported reaction of **10** with a group 15 precursor is that with the 1,3,5-triphosphabenzene, $P_3C_3Bu^t_3$ [53]. In this case, the only isolated product was the potassium salt of the 1,3-diphosphacyclopentadienyl anion, **30**, which was formed by abstraction of phosphorus from the



Scheme 8.



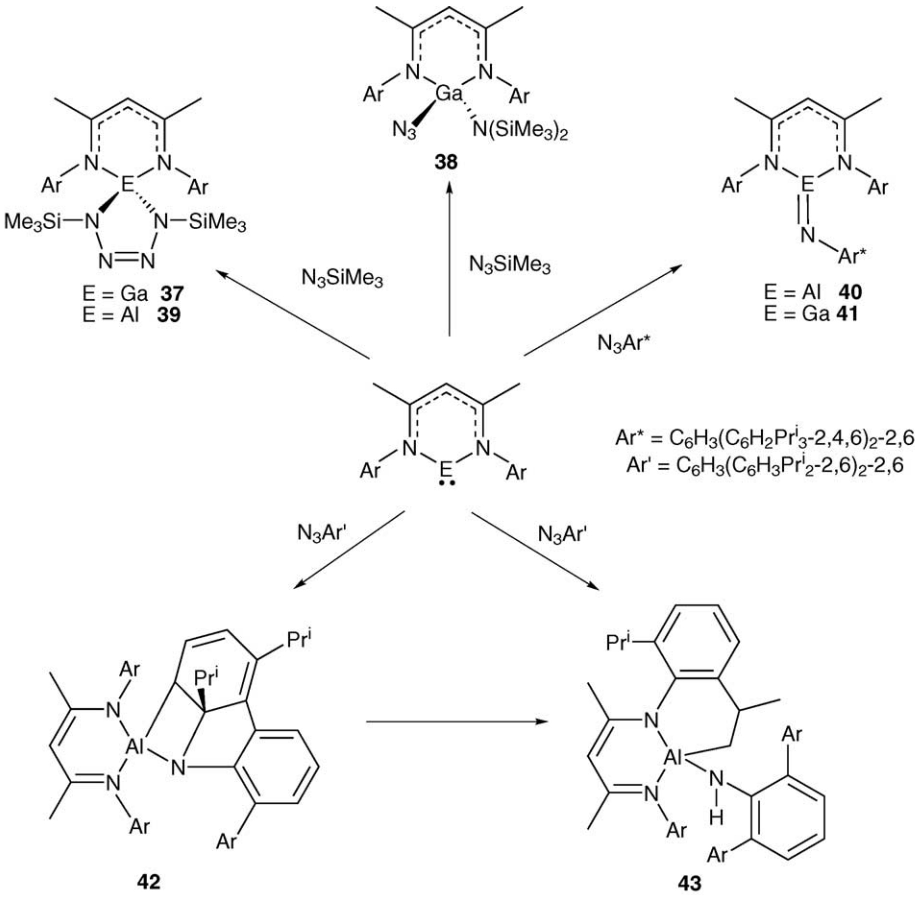
Scheme 9.

triphosphabenzene. This is an identical result to that from the reaction of potassium metal with $P_3C_3Bu^t_3$ [54] and highlights the strongly reducing nature of **10**.

The reactivity of NHCs with group 16 compounds is limited but these compounds are known to be readily oxidized with chalcogens to form the corresponding chalcogeno-ureas, [E = C{N(R′)C(H)}$_2$], E = O, S, Se or Te [8]. Similarly, when **10** is treated with sources of chalcogens its gallium centre is oxidised (Scheme 8) [38]. Two products from such reactions have been structurally characterised, **31** and **32**, and both were found to be dimeric, dianionic species. There are major differences, however, between the two structures in that the Ga_2Te_2 ring in **32** is symmetrical with almost equal Ga-Te distances [2.618 Å, avg.] that are consistent with single bonds. In contrast, the Ga_2O_2 ring in **31** is unsymmetrical and has long [1.905(3) Å] and short [1.814(3) Å] Ga–O bonds, the latter of which are suggestive of some double bonded character. The reactions of Ph_2E_2 (E = Se, Te) with **10** have also been investigated and, as expected, these led to oxidative insertions of the Ga(I) centre into the E–E bond of the dichalcogenide and the formation of the anionic complexes, **33** and **34**, both of which have been structurally characterised.

4.4. Reactions of neutral six-membered heterocycles with main group precursors

Whilst the transition metal coordination chemistry of the six-membered group 13 metal(I) heterocycles is limited, the

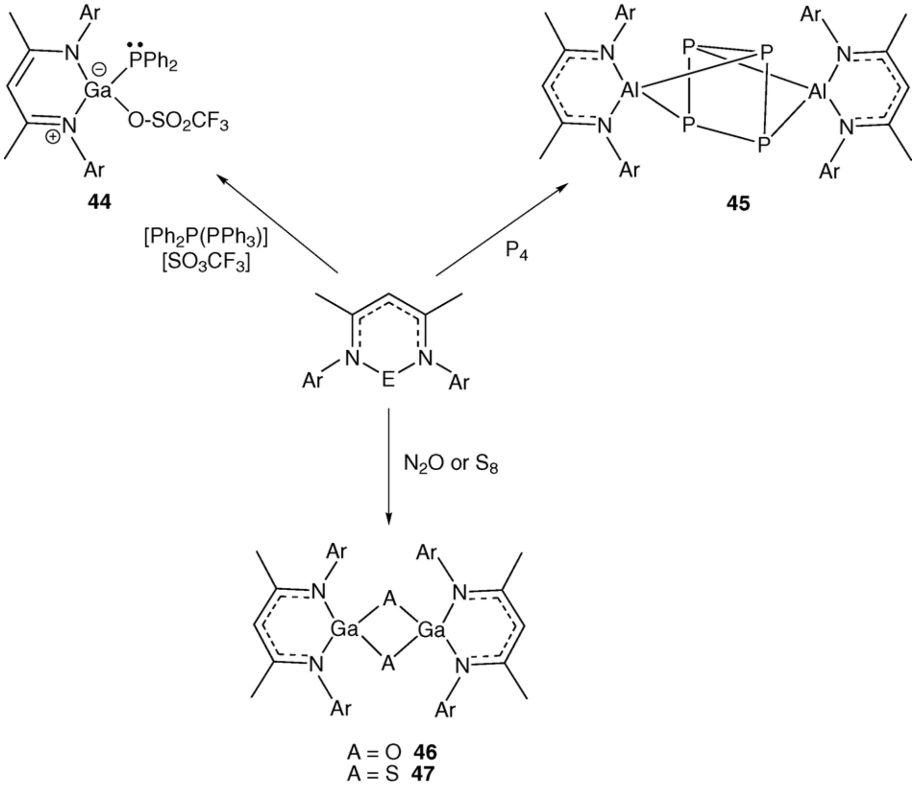


Scheme 10.

chemistry of their main group complexes has been more extensively investigated. In group 13, however, the only reported complex is the adduct of **12** with $B(C_6F_5)_3$, viz. **35** (Scheme 9) [55]. This compound has been used to gauge the strength of the donor–acceptor interactions in related low valent group 13 donor complexes of $B(C_6F_5)_3$ by examining the degree of pyramidalization at their boron centres. The results show that the order of increasing Lewis basicity is $Cp^*Ga < Ar^{\#}Ga < Cp^*Al < Ar'GaGaAr' \approx Ar^*Ga <$ **12**, $Ar^{\#}$: C_6H_3-2,6-(^{t}BuDipp)$_2$; Ar′: C_6H_3-2,6-Dipp$_2$; Ar*: C_6H_3-2,6-Trip$_2$; Dipp: 2,6-diisopropylphenyl; Trip: 2,4,6-triisopropylphenyl.

Little group 14 chemistry of **11** and **12** has come forward but that which has is confined to the aluminium heterocycle, **11** (Scheme 9). In an unusual reaction with an *N*-heterocyclic carbene, complex **36** forms as a result of a hydrogen migration from a methyl substituent to the Al centre [56]. Another unexpected outcome arose from the reaction of **11** with N_2CPh_2, a known source of the carbene,:CPh_2. This yielded the first diiminylaluminium compound, $[\{(Ph)_2CN\}_2Al\{[N(Ar)C(Me)]_2CH\}]$. In contrast, **11** has been found to be unreactive towards [2 + 1] cycloadditions with alkynes but the aluminacyclopropenes expected from these reactions, $[\{C(R){=}C(R)\}Al\{[N(Ar)C(Me)]_2CH\}]$, R = $SiMe_3$, Ph, etc., can alternatively be prepared in one pot potassium reductions of mixtures of an appropriate alkyne and $[I_2Al\{[N(Ar)C(Me)]_2CH\}]$ [57]. It is believed that the aluminacyclopropene is not formed via an in situ formation of the Al(I) heterocycle, **11**, but instead a radical process is involved. The aluminacyclopropenes are currently finding synthetic utility in a number of reactions [58].

Most of the reported main group chemistry of **11** and **12** comes from group 15. The reaction of **12** with Me_3SiN_3 in a 1:2 ratio gave a mixture of the tetrazole, **37**, and the amide/azide complex, **38**, presumably via a terminal imide intermediate (Scheme 10) [59]. Similarly, when **11** is treated with Me_3SiN_3 the analogous aluminium tetrazole **39** is formed [60]. When the more sterically bulky terphenyl azide precursor, Ar^*N_3, was used in these reactions the monomeric imide complexes, **40** and **41**, could be isolated without further association [61]. The ^{1}H and ^{13}C NMR spectra of **41** show that there is restricted rotation around the Ga–N(imide) bond, indicating a Ga–N π-bond has formed from overlap of gallium and nitrogen p orbitals. Only **41** has been structurally characterised and its structural features confirm multiple bond character in the Ga–N interaction. This bond is shorter than any other Ga–N bond and the imide nitrogen has a bent geometry, consistent with a stereochemically active lone pair. To further examine the multiple bond nature in this compound, restricted Hartree–Fock calculations were performed on the model complex, $[HN{=}Ga\{[N(H)C(H)]_2CH\}]$. The calculated optimum Ga–N(imido) distance compared very favourably to that observed in the structure of **41**, whilst the energy difference between planar and perpendicular Ga–N–H orientations was said to support the presence of a weak Ga–N π-bond. It is fascinating that the reaction of **11** with a slightly



Scheme 11.

different terphenyl azide, $Ar'N_3$, did not lead to a terminal imide complex, but instead gave a mixture of the two products, **42** and **43** (Scheme 10) [62]. Compound **42** is thought to be formed by a [2 + 2] cycloaddition of a phenyl ring of the Ar′ substituent with the Al=N bond of the presumed imide transient intermediate. Compound **43** can also be formed by thermal conversion of **42** and is believed to arise from C–H activation and hydrogen migration processes which are notionally similar to those proposed for the formation of **29**.

Two phosphorus complexes derived from reactions with **11** and **12** have been reported. In the first, the gallium heterocycle displaces PPh_3 from the phosphenium complex $[Ph_3P\text{-}PPh_2][OTf]$ to give **44** in a 69% yield (Scheme 11) [63]. This curious complex was structurally characterised and the triflate anion found to have a strong covalent interaction with the gallium centre. It was coined a “coordination chemistry Umpolung” as it involves donation from gallium, normally a electron acceptor, to a phosphorus centre, normally an electron donor. The other reaction involved the treatment of the aluminium heterocycle, **11**, with white phosphorus to give **45** [64]. The X-ray crystal structure of this compound revealed that two of the P–P bonds of the P_4 starting material had been opened, leading to two bridging aluminium heterocycles in the complex.

With respect to group 16 chemistry, the reactivity of **12** towards both N_2O or S_8 has been found to yield the dimeric compounds, **46** and **47**, which contain symmetrical Ga_2O_2 or Ga_2S_2 cores with essentially single Ga–chalcogen bond lengths (Scheme 11) [65]. The Ga–S–Ga angles in **47** are, however, more acute than the Ga–O–Ga angles in **46**, an observation which was ascribed to the relative reluctance of sulfur to hybridise.

5. Conclusions

The chemistry of compounds containing group 13 metals in a low oxidation state has provided some of the most fascinating results in main group chemistry in the past decade. This review has focussed on one aspect of this field; namely, the development of anionic five-membered and neutral six-membered heterocycles which formally contain a group 13 metal centre in the +1 oxidation. A variety of innovative synthetic routes to these heterocycles have been developed which has allowed a study of their coordination chemistry and further reactivity to commence. The results that have come forward in this arena to date have been novel and often unexpected. The chemistry of these heterocycles often mimics that of the important *N*-heterocyclic carbene class of ligand and/or that of group 13 diyl compounds. This is, however, not always the case and group 13 metal(I) heterocycles have exhibited a unique chemistry in many cases. The remarkable nature of the chemistry of these heterocycles that has come forward in just a few short years augers well for the future of this field. This will, no doubt, involve the appearance of important applications for the heterocycles and their complexes, as is already the case for compounds derived from *N*-heterocyclic carbenes.

Note added in proof

Since submission of this manuscript the reaction of the aluminium(I) heterocycly, **11**, with S_8 has been reported to yield the structurally characterised complex, $[\{(\mathbf{11})(\mu\text{-}S_3)\}_2]$, which was described as a homobimetallic derivative of the S_8 sulfur crown [66].

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